1UP

NASA TECHNICAL TRANSLATION NASA TT F 15,399

CATALYSIS AND LIFE-SUPPORT SYSTEMS IN OUTER SPACE

O. V. Krylov, V. A. Naumov and Yu. Ye. Sinyak

(NASA-TT-F-15399) CATALYSIS AND LIFE-SUPPORT SYSTEMS IN OUTER SPACE (Scientific Translation Service) ~~23~~ 21 p HC $4.25 CSCL 06K

N74-19762

Unclas
G3/05 34268

Translation of "Kataliz i sistemy zhizneobespecheniya v kosmose," Priroda, No. 10, Oct. 1973, pp. 2-9

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 APRIL 1974

CATALYSIS AND LIFE-SUPPORT SYSTEMS
IN OUTER SPACE

O. V. Krylov, V. A. Naumov and Yu. Ye. Sinyak*

The clear and faultless operation of spacecraft crew life support systems to a great extent depends on how all chemical services are set up in space. /2**

The conditions of realization of chemical reactions in the spacecraft are characterized by a number of peculiarities which distinguish them from reactions under ordinary, terrestrial conditions. For example, if it is necessary to carry out a reaction in a homogeneous medium, weightlessness significantly complicates separating or cleaning up the products of the reaction. However, weightlessness can also become a positive factor. In weightlessness for example (or with decreased gravitation), it is simpler to organize the process of removing solid products (if it is necessary) from a gas-flow reactor.

Economic prohibitions against conducting any particular chemical reaction in terrestrial practice could be lifted in space. Here one can fully use even the most expensive reagents if their total cost will comprise only an insignificant part of the cost of the entire space object. New limitations appear here, however. The requirement of high reliability with maximum limitation of weight, size and systems energy consumption is the foremost of these.

---

* V. A. Naumov, Yu. Ye. Sinyak, Candidates of Chemical Sciences

** Numbers in the margin indicate pagination of original foreign text.

Why is it necessary to conduct chemical reactions aboard the spacecraft?

In the program of the conquest of space an important place belongs to flights of manned spacecraft and stations. Systems to supply crews oxygen, water and food must be created not only for long flights to other plants of the Solar System, but also for the normal functioning of orbital stations. Although for /3
short-term flights one can limit the store of ready substances (water, oxygen, lyophilized* food), for long-term spaceflights (from several months to several years duration), reserves can so increase launch weight that they lead to a cost increase in the flight or even make it impossible. Moreover, the atmosphere of the spacecraft cabin must be purified of harmful substances which are excreted in the process of human vital activity (Figure 1).

Attempts to realize a closed cycle of substances in the hermetically sealed cabin by using plants and animals are at present far from resolution**.

Of the chemical reactions employed in life support systems, the catalytic processes are particularly effective.

Notwithstanding the appearance of a number of new methods of realizing chemical reactions (radiation chemistry, plasma chemistry, etc.), the role of catalysis in practice is not decreasing, but increasing. The development of the theory and practice of catalysis is leading to a constant increase not only

---

* Lyophilized food is food in the form of solutions, creams, jelly and other such products.

** V. V. Parin, I. M. Khazen, F. P. Kosmolinskiy. "Man in Space: Physiology and Psychology. Priroda, No. 4, 1971.

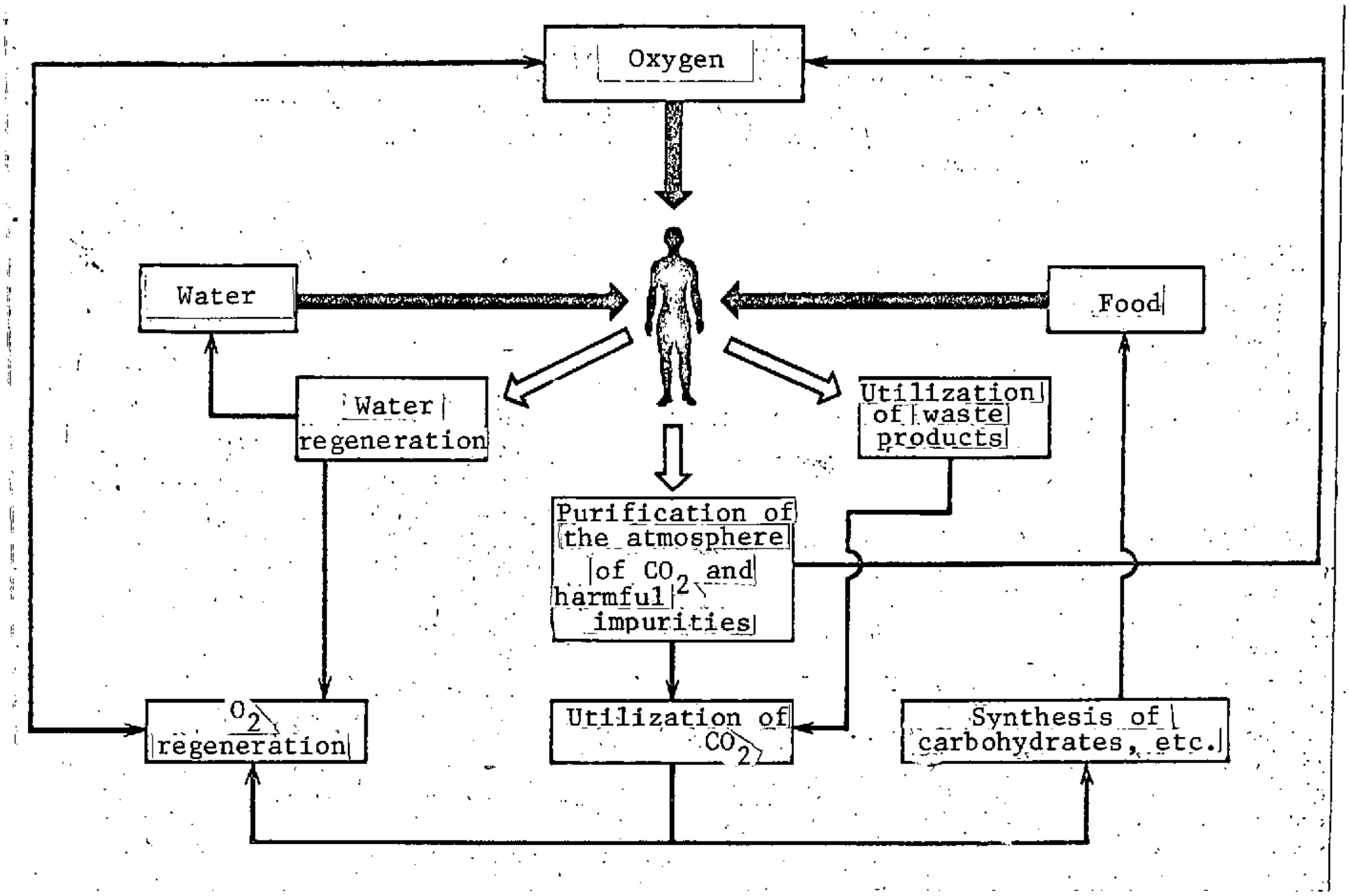

Figure 1. Diagram of purification and utilization in the spacecraft. The heavy lines show products for supporting the vital activity coming to the cosmonaut (food, water, oxygen); the lighter lines show metabolic products.

in the absolute scale, but also in the relative importance of catalytic production in the chemical industry. The use of catalysis in the spacecraft is natural, since this method permits one most effectively to transform a large number of substances by the aid of catalysts, whose weight is very small in comparison with the weight of reactants.

Catalysis and the Purification of Water

The regeneration of water from urine and other moisture-containing sources (sanitary-hygenic use water, the condensate of atmospheric moisture in the hermetically sealed cabin) brings the greatest economy in launch weight of the spacecraft. To purify water it is necessary to oxidize all organic impurities with the formation of CO_2, H_2O, SO_2, nitrogen or its oxides, with their subsequent removal or use. It is easiest to carry out such a reaction by means of evaporating the water and passing the water vapor with its impurities through deep-oxidation catalysts. /4
Catalytic methods can be realized by the use of vacuum distillation under atmospheric pressure.

In practice, two methods are used*.

The first method is evaporation at decreased pressure ($\sim$65 mm Hg), and consequently, at low boiling points, and leads to a decrease in the concentration of volatile organic substances in the vapor-gaseous phase. Catalytic oxydation must be carried out at a high temperature, using oxygen in place of air for deep oxidation. Carrying out the process of condensation with simultaneous decanting of the liquid in weightlessness and in a vacuum causes great technical difficulties.

Evaporation, catalytic oxydation and condensation occur significantly easier under atmospheric pressure. No autonomous stores of oxygen are required, inasmuch as cabin air is used for oxidation. Active oxide catalysts enable one to carry out the oxidation process at 150° C. Such a regeneration system can operate

* Sinyak, Yu. Ye., and S. V. Chizhov. In the Collection: Problemy kosmicheskoy biologii (Problems of Space Biology), Vol. 3, 1964.

both in the closed circuit regime, when air passes from the condensator to the evaporator inlet, and in the open variant using cabin air.

Each of the variants has its own advantages and disadvantages. The closed variant is safer — here the "breakthrough" of unreacted substances is a terrible event.

The effectiveness of the catalytic method was shown in a year-long medical-technical experiment which was discussed in detail in our press *. Over the course of a year three investigators consumed water regenerated from their urine by the catalytic method. During this process the catalysts had to function under extremely complex conditions — with elevated humidity, and a varied assortment of organic substances subject to oxidation. Moreover, the original product (urine, for example) is a labile substrate whose properties change with time.

For a further decrease in energy expenditure an assortment of low temperature catalysts is required, specifically those which would operate in the liquid phase.

Catalysis and the Conversion of Solid Wastes

The solid wastes of vital activity — feces, plant tops — can also be converted into simple compounds — CO_2, SO_2, ashes, etc. which can be used in the subsequent cycle of substances. For this purpose pyrolysis (gasification) of the solid wastes is carried out with subsequent oxidation of the organic compounds to the

* Burnazyan, A. I., et al. In the Book: Aviatsionnaya i kosmicheskaya meditsina (Aviation and Space Medicine), Vol. I, Moscow, 1969.

simplest oxides in the presence of heterogenic catalysts. In this case, particularly high requirements are made on the catalysts. They must function selectively and must be resistant to contamination, since sulphur compounds and other compounds which are typical catalytic poisons are formed during pyrolysis.

The products of conversion of solid wastes — carbon dioxide gas and mineral salts — can be used in systems which contain a biological component. For example, the ash which remains after catalytic combustion can be dissolved in nitric acid. The latter, in its turn, can be obtained catalytically from urine — by the breakdown of urea by the aid of the enzyme urease, or by the thermal decomposition of urea with the formation of CO_2 and ammonia; the latter is further oxidized on a platinum catalyst. Since mixtures of ammonia also contain catalytic poisons, selecting catalysts resistant to poisoning is of great significance.

Salt nutrient solutions prepared from ash and nitric acid are suitable for growing lower and higher plants, according to the data of biological estimates.

Catalysis and Atmospheric Regeneration

It is necessary to maintain a certain gaseous composition in the spacecraft cabin by adding oxygen and removing moisture, carbon dioxide gas and harmful impurities. Such harmful impurities as CO, CH_4, hydrogen, acetone, NH_3, etc. can be oxidized by cabin atmospheric oxygen in the so-called catalytic burners to CO_2, H_2O, and N_2. Various oxide mixtures of transitional metals (for example, hopcalite, which has been used in gas masks) and precious metals on carriers (for example, platinum) are used as catalysts.

The latter can also be used for fine catalytic purification of hydrogen of oxygen impurities (and oxygen of hydrogen impurities) in the process of electrolytic decomposition of water.

A man expires 20-25 carbon dioxide gas per hour. It is primarily necessary to regenerate oxygen from the carbon dioxide gas. With respect to the carbon, in the ideal one should strive to convert it into useful products. At this stage of development of technology, however, one can limit oneself to converting the carbon to a certain "terminal" substance which can be ejected from the spacecraft (or stored).

Although it is possible to obtain O_2 directly from CO_2, (electrical discharge, photocatalysis, etc.), of greatest significance are methods in which water is formed intermediately and subjected to electrolytic decomposition into oxygen and hydrogen, and the latter is used to hydrogenate the carbon dioxide gas:

$$CO_2 \xrightarrow{H_2} A + H_2O$$
$$H_2O \rightarrow H_2 + {}^1/_2O_2,$$

where A is carbon or the product of CO_2 hydrogenation. Dependent on the form of substance A, this process can be either single- or multi-stage.

We shall examine several variants of catalytic hydrogenation of CO_2 which are discussed in the literature.

1. A-methane. The reaction of carbon dioxide gas methanation occurs at a temperature above 200° C in the presence of several catalysts, the best of which are ruthenium and nickel on carriers:

$$CO_2+4H_2=CH_4+2H_2O.$$ /5

The reaction is exothermal. Depending on the design of the reactor, it is possible to realize several different regimes of the process — from the isothermal to the autothermal — with a greater or lesser drop in temperature along the catalytic layer.

2. A-higher hydrocarbons. During the methanation of carbon dioxide with removal of methane from the system, 2 moles H_2 are lost for each mole of CO_2. This leads to an increase in the use of water to obtain the hydrogen needed to hydrogenate the CO_2. To decrease the consumption of hydrogen, it was suggested that Fischer-tropsch synthesis be used:

$$(2_n+1)H_2 + {}_nCO = C_nH_{2n+2} + {}_nH_2O$$
$$2_nH_2 + {}_nCO = C_nH_{2n} + {}_nH_2O.$$

Higher hydrocarbons C_nH_{2n+2} are obtained in which the ratio H:C strives toward 2 with an increase of n, i.e., the expenditure of hydrogen decreases. During this process CO can be obtained according to reaction

$$CO_2 + H_2 = CO + H_2O,$$

which occurs in the presence of various (iron-chromium oxide, for example) catalysts.

3. A-acetylene and benzene. If one changes the carbon from CO_2 into acetylene or benzene (H:C = 1), then as calculations show, the loss of hydrogen can be compensated for at the expense of the so-called metabolic water (excess water-about 300 g per day as the result of food oxidation). Acetylene can be obtained from methane by various methods for example by electro-cracking. Acetylene is easily polymerized into benzene at 650° over activated charcoal. To convert acetylene to benzene

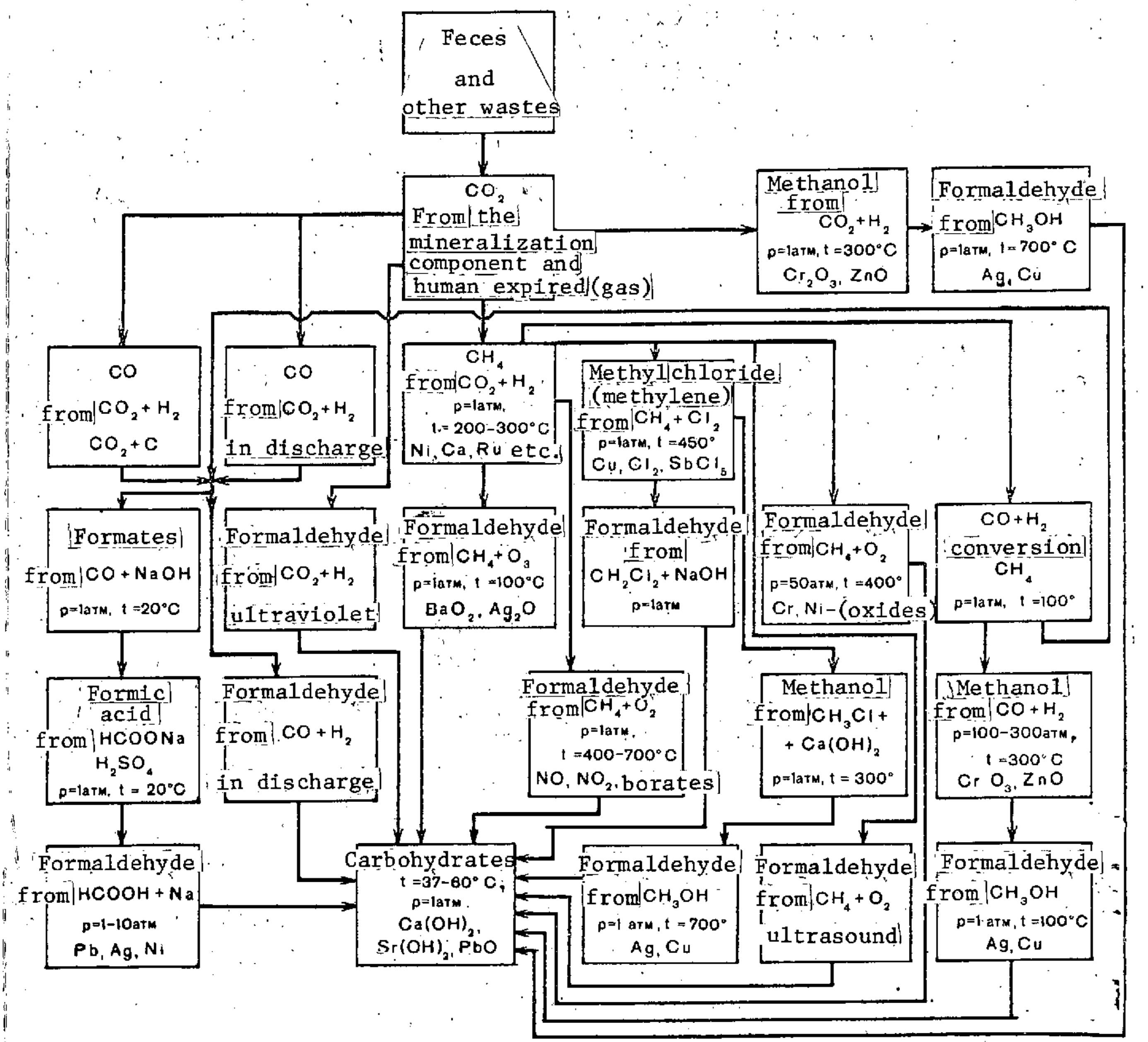

Figure 2. Possible diagram of staged physical-chemical synthesis of carbohydrates from products of human vital activity (metabolites). The diagram does not show the place of input of hydrogen, which participates in synthesis and which is obtained by the electrolysis of water, also contained in the waste products.

and styrene at low temperatures (60-70°), one can use homogeneous catalysts; the Ni or Co complexes. The advantage of the system in which benzene is obtained consists in the fact that benzene is more easily separated from unreacted substances and hydrogen than acetylene under conditions of weightlessness.

Hence, the system of regenerating oxygen from carbon dioxide gas with the discharge of benzene must include the following conversions: /6

$$
\begin{gathered}
CO_2 + 4H_2 = CH_4 + 2H_2O \\
2H_2O = 2H_2 + O_2 \\
CH_4 = {}^1/_2 C_2H_2 + {}^3/_2 H_2 \\
{}^1/_2 C_2H_2 = \frac{1}{6} C_6H_6
\end{gathered}
$$

$$CO_2 + {}^1/_2 H_2 = \frac{1}{6} C_6H_6 + O_2.$$

4. A-carbon. The catalytic cracking method

$$CH_4 = C + 2H_2$$

enables one to obtain solid carbon which can be removed from the system. In the presence of catalysts (Ni, Fe, and others), one can obtain equilibrium values of the degree of methane conversion. Thus, at 900° methane decomposes to carbon at a level of 95%. At lower temperatures it is necessary to employ recirculation or gas separation (separation of hydrogen from methane).

CO_2 hydrogenation and methane cracking lead to total conversion (i.e., the "Bosh process")

$$CO_2 + 2H_2 = 2H_2O + C.$$

This process can also be realized in a single reactor in the presence of recirculation with ejection of water from the cycle. Dependent on the catalyst, pressure and the amount of recirculation, the process is carried out at temperatures ranging from 500 - 750° C.

It is suggested that the Bosh process be carried out in stages:

$$1)\ CO_2 + H_2 = CO + H_2O$$
$$2)\ CO + H_2 = C + H_2O,$$

or

$$2a)\ 2CO = C + CO_2.$$

Exothermic reactions 2 and 2a occur with a high degree of conversion at a temperature below 500° in the presence of various catalysts, the best of which are Fe, Co, and Ni. When carrying out the Bosh process in stages, it is unnecessary to carry out each stage in a separate reactor; one can, as was suggested by associates of the Battelle Institute (USA), carry out the process in a single reactor such that the first stage occurs on one catalyst in the part of the reactor having a higher temperature, while the second stage (carbon formation) occurs on another catalyst in the part of the reactor with a lower temperature.

It should be noted that reaction 2a can be used in systems in which the first stage is not CO_2 hydrogenation, but rather the decomposition of CO_2 into CO and O_2 (for example in a solid electrolyte electrolyzer).

Yet another variant of the system of utilizing CO_2 through carbon is obtained when one combines the reaction of CO_2

methanation with the reaction:

$$CO_2 + CH_4 = 2C + 2H_2O.$$

5. A = $CO+CH_4$ mixture. Thermodynamic calculations show that with appropriate selection of conditions, one can realize the conversion of CO_2 into a mixture of $CO+ CH_4$ (+ water separated in the refrigerator-separator) with minimum amounts of unreacted H_2 and CO_2. The idea of this variant consists in using metabolic water for obtaining an additional amount of hydrogen, and in ejecting from the spacecraft the mixture of gases with the atomic ratio C:H:O = x:y:z, corresponding to the ratio $C_xH_yO_z$ in the food products of the given food ration. Although a 100% removal of water from all moisture-containing products is hardly possible even in the future (one must take into account leaks of atmosphere as the result of incomplete sealing of the cabin, the necessity of unsealing certain compartments of the spacecraft; at any rate, for example, for the cosmonaut to enter open space, etc.), and this method of utilizing CO_2 deserves attention.

We also note that catalytic methods of regenerating the atmosphere can also be used in life support systems based on stored substances. Oxygen in bound form can be stored in the form of sodium chlorate (the so-called "chlorate candles"), or hydrogen peroxide, which easily decomposes in the presence of various catalysts:

$$2NaClO_3 = 2NaCl + 3O_2$$
$$H_2O_2 = H_2O + {}^1/_2O_2.$$

Associates of Johns Hopkins University (USA) suggested using hydrazine and nitrogen tetroxide as sources of nitrogen and oxygen:

$$N_2H_4 + N_2O_4 = 2N_2 + O_2 + 2H_2O.$$

Catalytic decomposition of hydrazine

$$N_2H_4 = N_2 + 2H_2$$

in the presence of solid bases can be used to obtain nitrogen (a component part of the spacecraft atmosphere) and hydrogen (for use in the CO_2 hydrogenation system).

Catalysis and Artificial Food

The creation of closed systems in which regeneration of not only water and oxygen, but also of food products would be realized is a matter for the extremely distant future. Even today, however, in analyzing life support systems for flights of more than a year's duration, the possibilities of only partial production of food products from products of human vital activity and waste products of the biological complex are being examined.

Carbohydrates occupy first place in the human food ration, with respect to weight (400-500 g per day). It is natural therefore, /7 that the efforts of chemists occupied with the cycle of substances in hermetically sealed objects have been directed toward a study of the possibility of synthesizing carbohydrates from products of human vital activity.

In the literature, only one way to obtain carbohydrates from simple molecules is known— the condensation of formaldehyde. As early as 1861, A. M. Butlerov discovered that formaldehyde, in the presence of alkalais, changes into a syrup-like mass which contains sugar. However, the mechanism and kinetics of this reaction, as well as the composition of the products, have remained little studied up to recent times.

Formaldehyde can be obtained from CO_2 by one of the following formulas:

$$CO_2 \rightarrow CH_4 \rightarrow HCHO$$

$$CO_2 \rightarrow CH_3OH \rightarrow HCHO$$
$$CO_2 \rightarrow CO \rightarrow HCHO.$$

Figure 2 shows certain possible line diagrams of staged physical-chemical synthesis of carbohydrates from products of human vital activity.

Figure 3 shows a block diagram of one of the possible variants of the system (for simplicity the contours are not shown here) of a heat-carrier with the heat exchangers, refrigerators, etc., /8
that connect to it.

Catalysts known up to now for condensing formaldehyde into carbohydrates — calcium hydroxide, strontium, thallium, lead — yield a syrup-like mass as the result of reaction; this mass contains a large number of substances, among which are 10-15 or more monosaccharides (glucose, fructose and other carbohydrates containing from 3 to 7 atoms C). The kinetic data indicate an autocatalytic mechanism of reaction: the sugars formed accelerate the condensation of formaldehyde.

Investigations of recent years in the USSR* lead to the discovery of a number of new catalysts — hydroxides of the rare-earth elements which have more selective action. In the presence of

---

* Krylov, O. V., Yu. Ye. Sinyak, A. A. Berlin and I. L. Shul'gina, "DAN SSSR", No. 3, 1971.

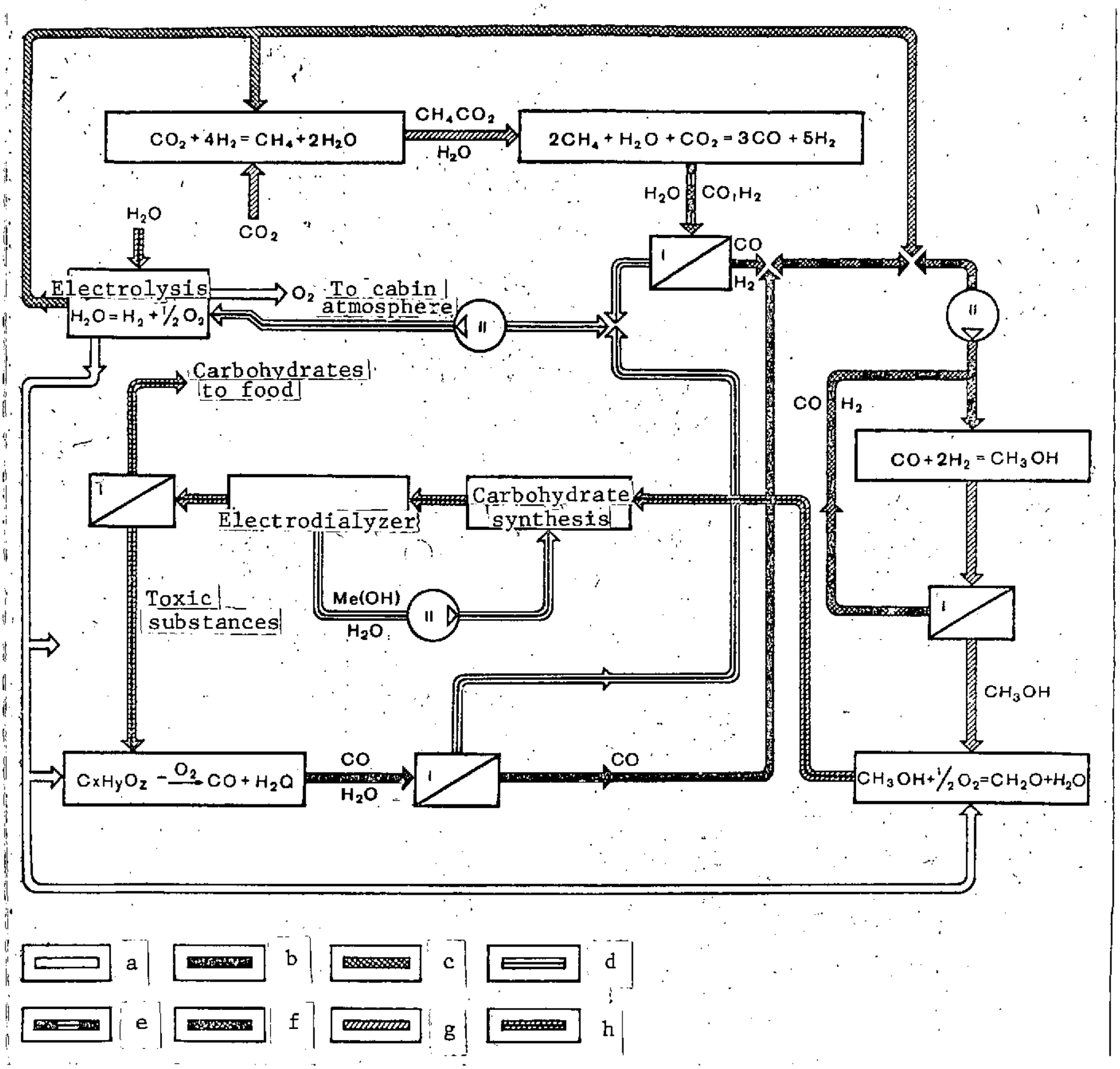

Figure 3. Block diagram of one of the possible variants of a system of carbohydrate synthesis in the spacecraft. Catalytic processes are going on in most of the compartments marked off by the outline. The transfer ducts for the different substances:

a- O_2, b- CO; c- H_2; d- H_2O; e- H_2O+CO; f- H_2+CO; g- h-other substances and mixtures. I- separator of substances (for example, a refrigerator - condensor); II- pump or compressor.

these catalysts, the number of sugars in the mixture obtained from formaldehyde decreases to 5-6. Even in this case, however, mixtures can be obtained which are toxic for the higher animals, and only certain bacterial cultures and plants can assimilate these mixtures. The low assimilability of the obtained syrups, besides the possible presence of unrecognized poisons, could be due to the fact that all sugars obtained from formaldehyde are optically inactive. They contain both optical antipodes of any particular sugar (for example, D-glucose and L-glucose), one of which could be useful for the organism and the other — harmful.

The stoichiometry of conversions in the system for regenerating oxygen from carbon dioxide and water with a yield of carbohydrates containing 6 atoms of C,-hexose is described by the equation:

$$CO_2 + H_2O = \frac{1}{6} C_6H_{12}O_6 + O_2.$$

Due to the difficulties which appeared with obtaining assimilable carbohydrates, certain investigators turned their attention to the possibility of obtaining simpler substances from formaldehyde and capable of assimilation by the organism, glycerin, for example. Investigations of the kinetics of formaldehyde condensation showed that the conversion of CH_2O into hexose occurs sequentially through sugars containing 2,3,4 and 5 atoms C. If one could halt the condensation reaction at the stage of three atoms C (a mixture of glyceraldehyde CH_2OHCH_2OHCHO with dioxyacetone $CH_2OHCHOCH_2OH$), and then hydrate this mixture on platinum black, one could obtain a 90% yield of glycerin. Toxicological experiments have shown that glycerin is assimilated by the organism. To make it more tasty, one can add a small amount of fruit syrups to the glycerin.

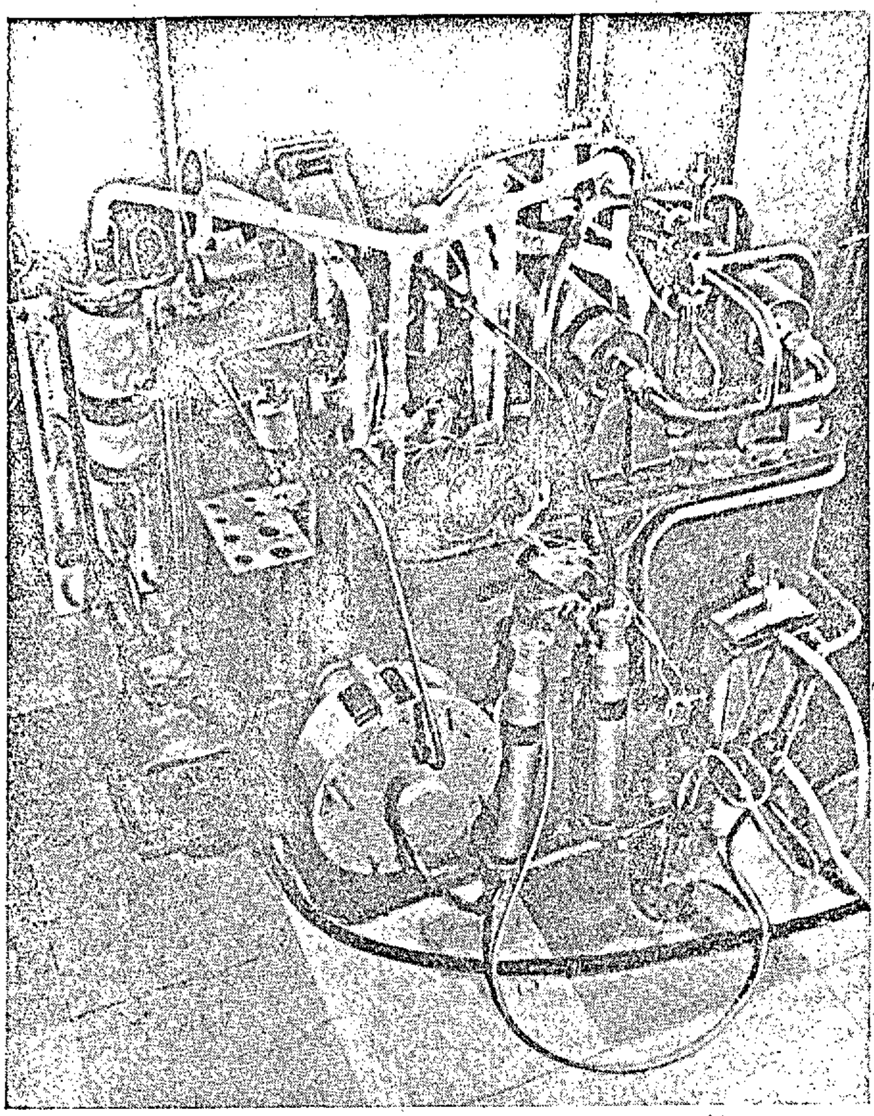

Figure 4. Prototype of an installation for regenerating water by the oxidation-catalytic method.

Another method of obtaining glycerin from formaldehyde and acetylene consists in a three-stage synthesis according to the following reactions:

$$HCHO + C_2H_2 = HCCCH_2OH$$
$$HCCCH_2OH + H_2 = CH_2 = CHCH_2OH$$
$$CH_2 = CHCH_2OH + {}^1/_2O_2 + + H_2O = HOCH_2CHOHCH_2OH$$

Certain Prospects

The reactions discussed above far from exhaust the entire multiplicity of variants of life support systems employing catalysis which are under examination at present. According to our reckoning, the number of such variants exceeds a hundred. As a result, one /9
can speak of a whole trend which has taken shape over the past decade, a trend in catalytic chemistry and in mixed technical fields related to the study of catalytic methods of converting substances in spacecraft crew life support systems.

When carrying out catalytic reactions in the spacecraft cabin, it is vital to take into account a number of requirements made on life support systems — high reliability, minimum energetic expenditures, minimum size and weight of the apparatus — as well as minimum service time by the operator, the capacity to combine with other systems and minimum levels of noise. These requirements can exert a significant influence on the selection of the thermal regime of a process, for example. Hence, the problem does not consist in optimizing the process as such, but in optimizing the process within the framework of the complex life support system.

One can also note the specific characteristics of carrying out the catalytic reaction in the spacecraft. Thus, weightlessness and decreased gravitation provide broad possibilities for using reactors with a moving layer of catalyst at significantly slower linear flow rates of reagents than is the case under terrestrial conditions with the fluidized bed of the catalyst. Great limitations can be imposed on the use of catalysts by vibration stresses. In connection with this, it is vital to develop catalysts with increased mechanical strength, and also to seek original designs for the configuration of catalytic layers.

When selecting any catalyst, it is necessary to take into account the need for increased periods of service, and therefore more attention should be paid to problems of catalyst poisoning and aging and to methods of regenerating them. Here the use of such classic methods of regenerating catalysts as blowing with a stream of air or water vapor with the goal of burning off carbonaceous deposits is not always possible, if only because this cannot be done with the use of very minute quantities of air or vapor.

The developed chains of conversion can be used in the future not only for spacecraft cabins, but also in other cases where it is necessary to have complete conversion without removing a substance from the cycle. For example, the question of the desirability of complete circulation of water and gases at chemical, paper-cellulose and other enterprises, with the goal of preventing pollution of the atmosphere and natural water, is presently being widely discussed. Certain of the methods found for spacecraft cabins will probably be used for terrestrial conditions as well. No matter how fantastic the problem of artificial synthesis of carbohydrates on a large scale may seem today, work should also be carried out in this realm, because it is difficult to predict the future conditions of food products. It is necessary to prepare various solutions for the XXI century now.

The vast development of space science and technology poses new and ever more complex problems before the different sciences with each passing year. Catalytic methods, being a powerful instrument in regulating the rate and direction of chemical conversions, will unquestionably find wide application in spacecraft systems.

RECOMMENDED LITERATURE

1. Tsiolkovskiy, K. E. Izbrannyye trudy (Selected Works). Moscow, 1962.

2. Tsiolkovskiy, K. E. Chelovek pod vodoy i v kosmose (Man under Water and in Space). A collection. Moscow, 1967.

3. Burnazyan, A. I., et al. A Year-Long Medical-Technical Experiment in a Terrestrial Complex of Life Support Systems. Kosmicheskaya biologiya i meditsina (Space Biology and Medicine), No. 1, 1969.

4. Voronin, G. I. and A. I. Polivoda. Spacecraft Crew Life Support. Mashinostroyeniye, Moscow, 1967.

5. Ivanov, D. I. and A. I. Khromushkin. The Human Life Support System in High Altitude and Space Flights. Mashinostroyeniye, Moscow, 1968.

6. Chizhov, S. V. and Yu. Ye. Sinyak. Vodoobespecheniye ekipazhey kosmicheskikh korabley (Spacecraft Crew Water Supply), Nauka Press, Moscow, 1973.

7. Manned Spacecraft: Engineering Design and Operation, N.Y. 1964.

8. Pearson, A. O. and J. K. Jackson. Summary of a 90-day Manned Test of a Regeneration Life Support System. XXII International Astronautical Congress, Brussels, 1971.

Translated for National Aeronautics and Space Administration under contract No. NASw 2483, by SCITRAN, P. O. Box 5456, Santa Barbara, California, 93108.